

## CATALYTIC LIQUEFACTION OF COAL

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### INTRODUCTION

Most catalytic liquefaction processes for producing low-sulfur liquid fuel from coal use large amounts of hydrogen which will have to be produced at high cost. In our previous work (1), we reported our attempt to use low-cost syngas to hydro-treat coal in the presence of added water, vehicle, and cobalt molybdate-sodium carbonate catalyst. Catalytic coal liquefaction using syngas reduces the capital and operating costs by eliminating shift converters and purifying systems needed for the liquefaction process using hydrogen. New catalysts have been prepared and tested with syngas to promote liquefaction and desulfurization as well as water-gas shift conversion. Cobalt molybdate catalyst impregnated with alkali metal compounds, such as potassium carbonate, sodium carbonate, and potassium acetate, exhibited good activities for these reactions.

The liquefaction of coal by syngas, like that by hydrogen, appears to proceed via production of asphaltene and conversion of the asphaltene to oil. Because of the important effect of asphaltenes on the viscosity of the product oil (2), the progress of asphaltene formation and asphaltene conversion during the coal liquefaction has been investigated, and some observations on the chemistry of asphaltenes are presented here.

### EXPERIMENTAL

The liquefaction of coal was studied in a magnetically-stirred autoclave. The experimental method is similar to that described earlier (1). The analyses of coal and vehicle used are shown in Table 1. Most coal liquefaction experiments used a liquid fraction (boiling point 270°-630°C) derived from the Solvent Refined Coal Process as the vehicle. For coal hydrotreating by hydrogen alone, the catalyst was a cobalt molybdate supported on alumina-silica (Harshaw CoMo 0402T, 3% CoO - 15% MoO<sub>3</sub>). For coal hydrotreating by syngas, the cobalt molybdate catalyst was impregnated with alkali metal compounds, such as potassium carbonate, sodium carbonate, and potassium acetate. The cobalt molybdate-alkali metal compound weight ratio was 2:1. Typically, 2.3 to 2.8 moles of reactant gas and 30 grams of coal as received were charged to the autoclave. The reaction was carried out in the temperature range of 400° to 450°C at about 3,000 psi in the presence of added water, vehicle, and catalyst. Total products were filtered at ambient or warmer temperature to obtain liquid oils. Asphaltenes, operationally defined as being soluble in benzene and insoluble in pentane, were isolated from the oil products according to procedures established by the Analytical Section of the Pittsburgh Energy Research Center. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, and asphaltene formed are given as weight percent based on moisture- and ash-free (maf) coal.

TABLE 1. Analyses of coal and vehicle, percent

	Coal				Vehicle	
	Kentucky	Bituminous	W. Virginia	Bituminous	Alkyl-naphthalene	SRC
	As used	maf	As used	maf		liquid
C	58.8	75.9	73.0	80.9	90.6	88.8
H	4.9	5.4	5.3	5.7	8.7	7.4
N	1.2	1.6	1.3	1.4	0.06	1.1
S	5.16	6.67	3.80	4.21	0.37	0.65
O	14.4	10.5	8.6	7.9	0.27	2.1
Ash	15.5		8.1			0.03
Moisture	7.1		1.7			
VM	35.7	46.1	43.3	48.0		
Btu/lb	11,500		12,900			
Asphaltene					0.8	7.1
H/C ratio		0.85		0.84	1.15	1.00

## RESULTS AND DISCUSSION

Hydrotreating of Coal. New catalysts were prepared and tested with syngas for coal liquefaction. Catalysts were cobalt molybdate impregnated with alkali metal compounds such as potassium carbonate, sodium carbonate, and potassium acetate. Table 2 shows the results of hydrotreating West Virginia bituminous coal at 450°C by 2H<sub>2</sub>:1CO syngas. The amount of water added was 10 parts per hundred parts of coal plus vehicle, corresponding to 0.7 mole of steam per mole of CO in the reactor. The results obtained with various catalysts were quite satisfactory.

TABLE 2. Hydrotreating of West Virginia bituminous coal<sup>a</sup>

(Coal:SRC liquid = 1:2.3, 450°C, 15 min.)

Feed gas	Syngas (2H <sub>2</sub> :1CO)				H <sub>2</sub>
	K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	CoMo-Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	CoMo-KOAc <sup>c</sup>	CoMo <sup>d</sup>
Catalyst					
Water added, parts/100 parts coal + vehicle	10	10	10	10	
Operating pressure, psi	3,100	3,000	3,000	2,800	2,800
Conversion, %	93	95	94	96	94
Oil yield, %	59	68	64	70	71
Asphaltene formed, %	62.9	42.2	52.8	55.5	30.3
S in oil product, %	0.67	0.40	0.45	0.50	0.39
Kinematic viscosity, cst at 60°C	44	20	22	22	15
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	5.4	8.6	10.5	11.5	10.7

<sup>a</sup> Data are given in weight percent of maf coal.<sup>b</sup> One part per hundred parts coal plus vehicle.<sup>c</sup> Three parts per hundred parts coal plus vehicle.<sup>d</sup> Two parts per hundred parts coal plus vehicle.

Figure 1 shows the increase of syngas or H<sub>2</sub> consumption with increasing reaction temperature and time. CoMo impregnated with K<sub>2</sub>CO<sub>3</sub> was used as the catalyst in the syngas runs. Regardless of the reaction temperature and time, the asphaltene content of the oil product decreases with the increase of the syngas or H<sub>2</sub> consumption as shown in Figure 2. In general, the sulfur content and the oil viscosity also decrease with the increase of the syngas or H<sub>2</sub> consumption. Thus further improvements in the oil quality by reduction in asphaltene and sulfur contents could be attained at the expense of oil yield under more severe conditions at 450°C and increased reaction time as shown in Table 3. However, both syngas and H<sub>2</sub> usage would increase substantially. It would not be a major problem if low cost syngas were used in the liquefaction process, but it could be too costly if H<sub>2</sub> were used. It is noteworthy that one objective of the SYNTHOIL process (3) is to convert coal to a low-sulfur liquid fuel with minimum consumption of high cost H<sub>2</sub>.

TABLE 3. Effect of reaction time on hydrotreating of coal<sup>a</sup>

(Coal:SRC liquid = 1:2.3, 450°C)

Catalyst	Syngas (H <sub>2</sub> :CO = 2:1)		H <sub>2</sub>	
	CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>		CoMo <sup>c</sup>	
Reaction time, min.	30	60	30	60
Water added, parts/100 parts coal + vehicle	10	10		
Operating pressure, psi	3,000	3,000	2,700	2,800
Conversion, %	94	95	95	95
Oil yield, %	65	42	59	48
Asphaltene formed, %	38.2	32.2	14.8	14.7
S in oil product, %	0.43	0.32	0.31	0.26
Kinematic viscosity, cst at 60°C	16	9	10	7
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	11.2	16.2	13.7	16.1
CO/H <sub>2</sub> consumption ratio	1.4	0.8		
H <sub>2</sub> /CO ratio of off-gas	4.3	3.2		

<sup>a</sup> Data are given in weight percent of maf coal.

<sup>b</sup> Three parts per hundred parts coal plus vehicle.

<sup>c</sup> Two parts per hundred parts coal plus vehicle.

Table 4 shows the hydrotreating of coal at various temperatures at which the consumption of syngas and H<sub>2</sub> would be 4,000 to 5,500 scf per barrel of oil, the normal range for a process. The asphaltene and the sulfur contents of the oil products obtained in the syngas and H<sub>2</sub> runs are comparable. Under these conditions, the syngas usage was in the range of 3,900 to 4,700 scf per barrel of oil as compared to the H<sub>2</sub> usage of 4,700 to 5,500 scf per barrel when pure H<sub>2</sub> was used. Use of 1H<sub>2</sub>:1CO syngas in place of 2H<sub>2</sub>:1CO syngas gave no significant difference in the results except that the H<sub>2</sub>/CO ratio of off-gas and CO/H<sub>2</sub> consumption ratio varied.

TABLE 4. Hydrotreating of coal at various temperatures<sup>a</sup>

Catalyst	(Coal:SRC liquid = 1:2.3)									
	Syngas (H <sub>2</sub> :CO = 1:1)					Syngas (H <sub>2</sub> :CO = 2:1)				
	CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>					CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>				
Temperature, °C	400	425	450			400	425	450		
Time, Min.	60	30	15			60	30	15		
Water added, parts/100 parts coal + vehicle	10	10	10			10	10	10		
Operating pressure, psi	3,100	3,100	3,100			3,000	3,100	3,000		
Conversion, %	89	95	93			89	94	95		
Oil yield, %	73	65	64			71	70	68		
Asphaltene formed, %	57.2	51.4	53.2			48.9	53.7	42.2		
Oil analysis, %										
C	88.2					88.1		88.5		
H	7.5					7.5		7.5		
N	1.2					1.2		1.2		
S	0.54	0.47	0.47			0.53	0.51	0.40		
O	2.6					2.7		2.4		
Kinematic viscosity, cst at 60°C	45	25	21			38	28	20		
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	7.8	9.9	10.3			7.5	9.2	8.6		
CO/H <sub>2</sub> consumption ratio	15	23	6.1			3.2	2.2	2.1		
H <sub>2</sub> /CO ratio of off-gas	1.8	2.1	2.1			3.4	4.4	4.1		

<sup>a</sup> Data are given in weight percent of maf coal.

<sup>b</sup> Three parts per hundred parts coal plus vehicle.

<sup>c</sup> Two parts per hundred parts coal plus vehicle.

**Formation of Asphaltene.** The coal liquefaction by syngas, like that by  $H_2$ , proceeds via production of asphaltene. The decrease in the asphaltene formation with the increase in the syngas consumption (Figure 2) indicates that the asphaltene formed is converted to oil under further hydrotreating. Sternberg et al. (2) reported a significant effect of asphaltenes on the viscosity of the SYNTHOIL product oil. We also found that the viscosity of the oil product correlates well with its asphaltene content, regardless of the reaction temperature and time (see Figure 3). A similar relationship is also observed when pure  $H_2$  is used. The difference in the curves obtained from syngas and  $H_2$  runs is probably attributable to the difference in the molecular structure and size of asphaltenes obtained (see below).

Because of the important effect of the amount and the type of asphaltene on the property of the liquefied product, studies were conducted on the formation of asphaltene and oil during the progress of coal liquefaction. Kentucky bituminous coal was liquefied in the presence of an asphaltene-free alkyl naphthalene-based vehicle oil in both syngas and  $H_2$  systems. Catalysts were  $CoMo - Na_2CO_3$  and  $CoMo$  for syngas and  $H_2$  runs, respectively. An operating pressure of about 3,000 psi and reaction temperatures of 400° to 450°C were used. It required about 60 to 70 minutes for the autoclave to reach desired temperatures. The moment the desired temperature was reached was taken as zero time.

Figure 4 shows the results at 400°C. Nearly 30% of the conversion occurred before the autoclave reached the temperature in both syngas and  $H_2$  runs. As viewed by earlier workers (4), the rate of coal conversion to asphaltene is far greater than the rate of asphaltene hydrogenation to oil, and the asphaltene formation goes through a maximum with respect to time. The hydrogenation of asphaltene to oil at 400°C is very slow and substantial parts of the conversion product — equivalent to about one-third of maf coal — still remained as asphaltene after 120 minutes. At 450°C, the asphaltene formation appears to reach a maximum rapidly but decreases relatively slowly by hydrotreating (see Table 5). The rates of asphaltene formation and asphaltene conversion are relatively greater in the coal liquefaction by  $H_2$  than by syngas.

TABLE 5. **Formation of asphaltene during coal liquefaction**

(Kentucky bituminous coal:alkyl naphthalene = 1:2.3, 2,900 psi, 450°C)

	Syngas ( $2H_2:1CO$ )			$H_2$		
Reaction time, min.	5	15	60	5	15	60
Asphaltene formed, % <sup>a</sup>	42.6	38.0	25.5	47.1	26.7	6.7
Asphaltene analysis, %						
C	84.1	85.8	87.0	85.4	87.1	86.9
H	6.3	6.3	5.0	6.5	6.3	5.7
N	1.6	2.1	2.0	1.5	2.0	2.1
S	1.3	0.15	0.4	0.64	0.23	0.36
O	7.0	5.7 <sup>b</sup>	4.0	6.0	4.3 <sup>b</sup>	5.1
Molecular weight of asphaltene	387	430	407	457	573	597

<sup>a</sup> Weight percent of maf coal.

<sup>b</sup> By difference.

It is interesting to note that, under similar liquefaction conditions, molecular weight (number average) of the asphaltene formed under syngas is lower than that of the asphaltene formed under  $H_2$  (see Table 5). The molecular weight was determined by vapor pressure osmometry of the asphaltene in benzene. Table 6 shows molecular weights of asphaltene and total oil products obtained from the

liquefaction of West Virginia bituminous coal. Except where specified a cryoscopic method was used. Again, the molecular weight of asphaltene is lower when syngas is used. This suggests that the size of asphaltene molecules obtained in the syngas system is smaller, and this could, at a given asphaltene content, result in lower oil viscosity in the syngas system than in the  $H_2$  system (see Figure 3).

TABLE 6. Molecular weights of oil products and asphaltenes

(West Virginia bituminous coal:SRC liquid = 1:2.3, 450°C, 3,000 psi)

Time, min.	Syngas ( $2H_2:1CO$ )		$H_2$	
	Molecular weight <sup>a</sup>		Molecular weight <sup>a</sup>	
	Asphaltene	Oil product	Asphaltene	Oil product
15	339 <sup>b</sup>	218	437 <sup>b</sup>	227
30	494	221	544	210
60	395	194	405	194

<sup>a</sup> By cryoscopic method.

<sup>b</sup> By osmometry.

Liquefaction Process Using Syngas. In evaluating a coal liquefaction process using syngas, a modification of the SYNTHOIL process was considered. A schematic flow diagram is shown in Figure 5, and the gas stream flows in scfh (on 100 lb/hr maf coal basis) and volume percent are shown in Table 7. It is assumed that the process is operated at 3,000 psi and 450°C and that the syngas flow rate is at a feed gas/coal-oil slurry volume ratio of 5.9. These operating conditions will result in turbulent flow in a packed-bed reactor. Since syngas has a higher density than  $H_2$ , a lower volumetric flow is necessary than that of  $H_2$  in the SYNTHOIL process. The syngas leaving a gasifier with the equilibrium composition at 1800°F ( $H_2/CO = 0.53$ ) is introduced to the recycle gas ( $H_2/CO = 3.4$ ) to make up the feed gas ( $H_2/CO = 2$ ). Steam is introduced to the feed gas to give an  $H_2O/CO$  mole ratio of 0.7, corresponding to the autoclave conditions. The flow and composition of the off-gas (Stream 3) were estimated from vapor-liquid equilibria of various components with the liquid oil at the receivers. A small amount of the recycle gas can be removed, if necessary, to keep the methane level from building up. The syngas consumption is about 4,500 scf per barrel of oil when the oil yield is 3.5 barrels per ton of coal (as received). Since the syngas produced from the gasifier is used directly, shift converters and purifying systems required in the SYNTHOIL process can be eliminated.

TABLE 7. Gas stream flows

(Basis: 100 lb/hr maf coal feed to process)

Stream	Gas composition, mole percent				
	1	2	3	4	5
$H_2$	46.4	47.6	15.8	61.7	30.6
CO	22.7	14.7	13.5	18.1	58.3
$CH_4$	12.2	15.4	20.7	18.4	0
$C_2H_6$	1.2	1.9	6.9	1.8	0
$H_2S$	0.2	0.5	1.8	0	1.3
$CO_2$	1.6	12.9	41.3	0	8.7
$H_2O$	15.7	7.0	0	0	1.1
Flow, scfh	4774.7	4206.4	336.7	3162.9	873.6

The thermal balance of the process is shown in Figure 6. The calculation was based on 100 Btu input of coal. Heating values are: coal as received = 12,900 Btu/lb, oil = 17,000 Btu/lb, recycle gas = 475 Btu/scf, and off-gas = 439 Btu/scf. The overall thermal efficiency was calculated to be 76.6%.

#### CONCLUSIONS

Liquefaction of high sulfur bituminous coal at 3,000 psi under syngas in the presence of steam, recycle vehicle, and cobalt molybdate catalyst impregnated with potassium carbonate gives high coal conversions and oil yields at 400° to 450°C. The asphaltene, the sulfur content, and the viscosity of the oil products decrease with increasing consumption of syngas, and the syngas consumption increases with increasing reaction temperature and residence time. When syngas is used in place of hydrogen in coal liquefaction, the rate of asphaltene conversion to oil is slower but asphaltenes formed have molecules of smaller sizes.

A catalytic coal liquefaction process using syngas gives high thermal efficiency and reduces the capital and operating costs by eliminating shift converters and purifying systems.

#### ACKNOWLEDGEMENT

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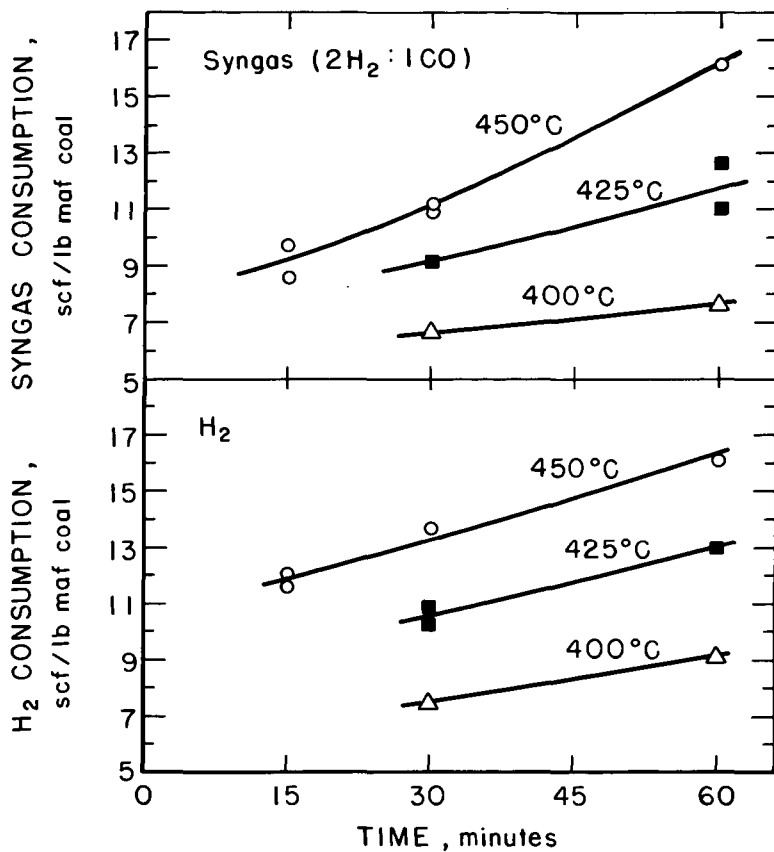


Figure 1 - Change of syngas or  $H_2$  consumption with temperature and time.

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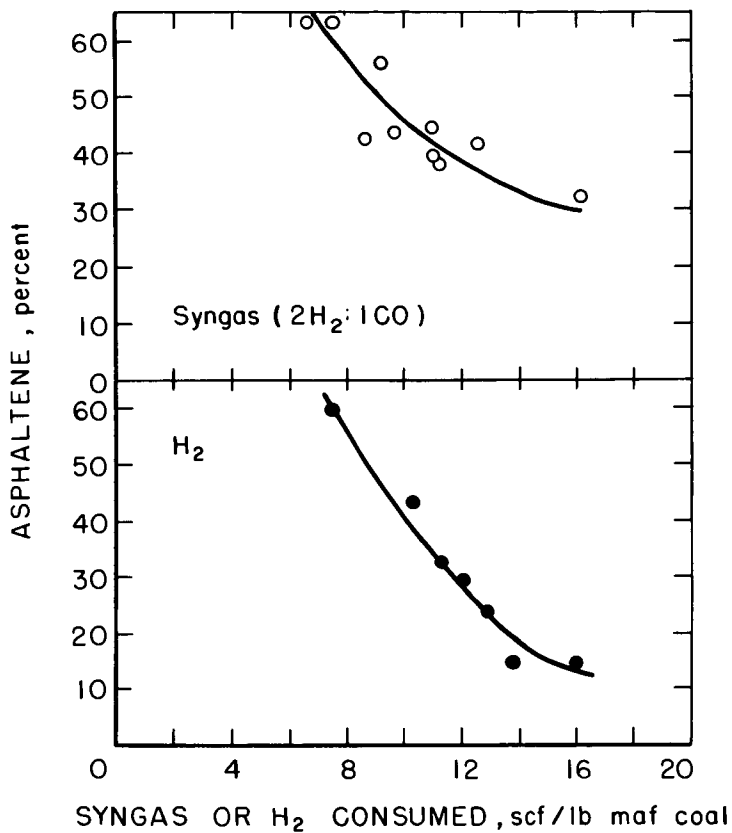


Figure 2 - Decrease of asphaltene with syngas or H<sub>2</sub> consumption.

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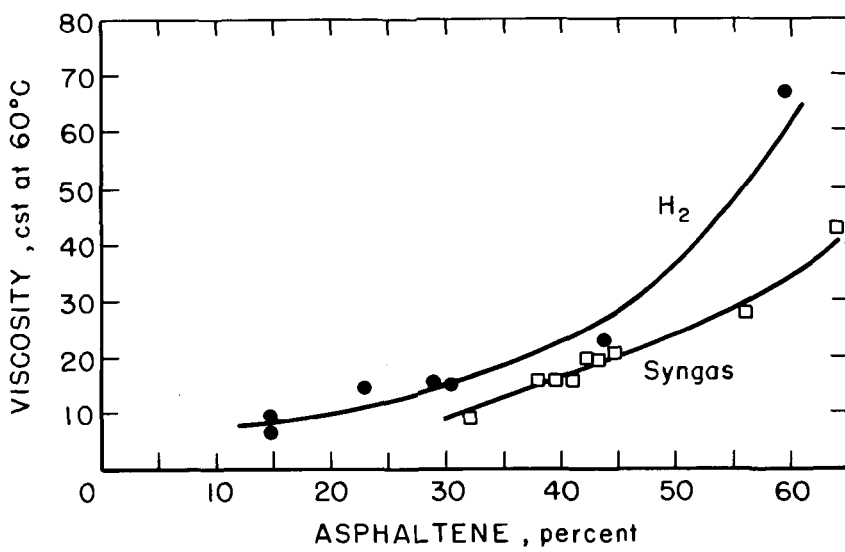


Figure 3- Oil viscosity vs asphaltene content .

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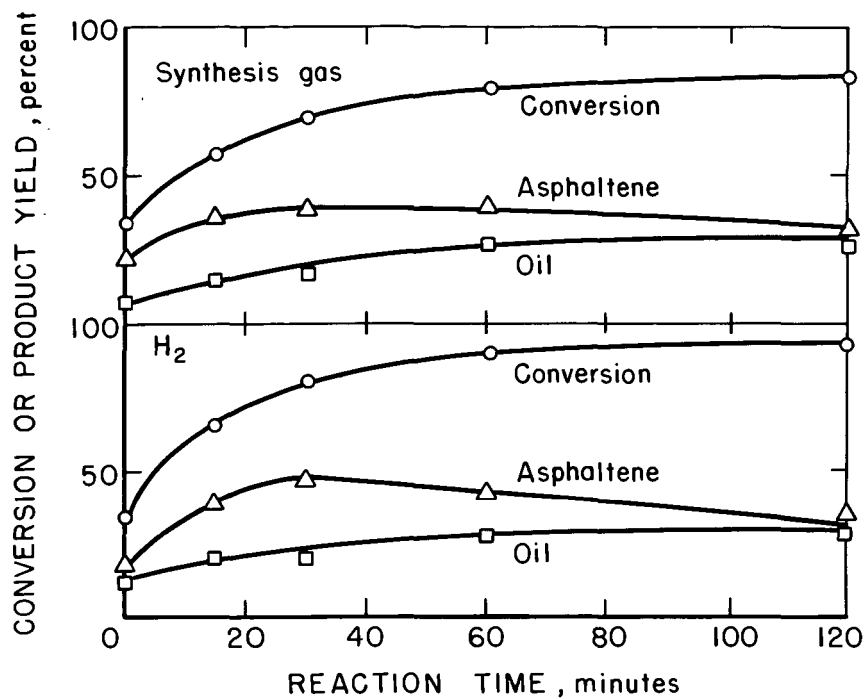
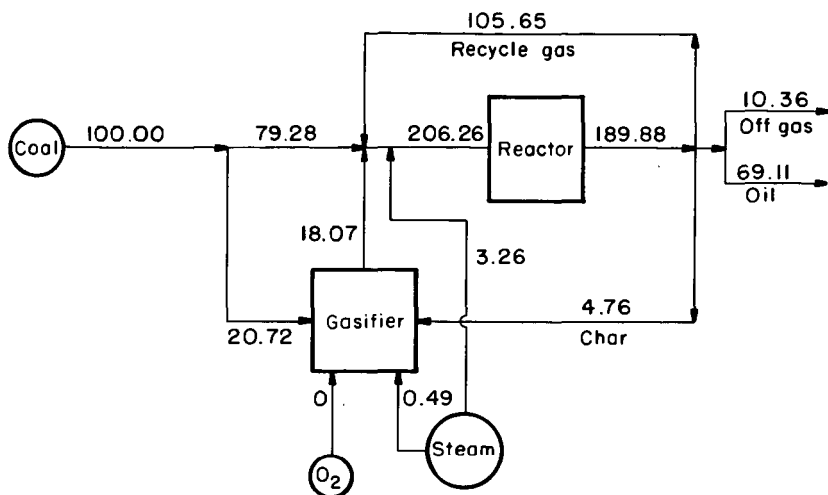


Figure 4 - Conversion and product yield vs reaction time at 400°C .

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$$\text{Thermal efficiency} = \frac{69.11 + 10.36}{100 + 0.49 + 3.26} = 76.6\%$$

Figure 6 - Thermal balance of liquefaction process (basis: 100 Btu input of coal).

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